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THE REACTION OF OXYGEN ATOMS WITH NITRATES.(U)
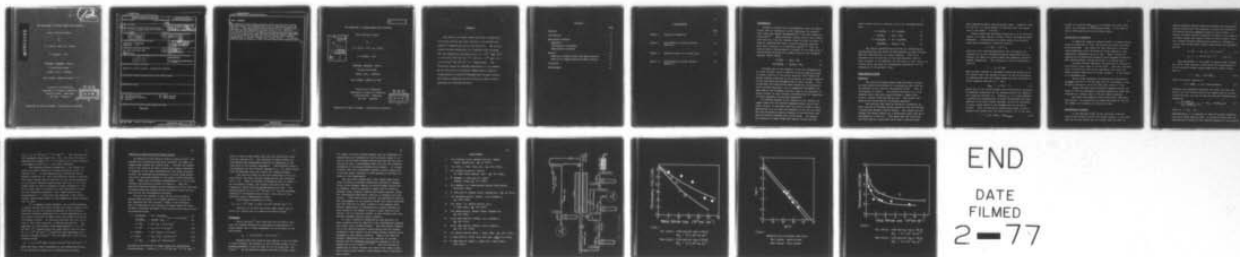NOV 76   B A THRUSH, L F SALTER   DA-ERO-75-G-020

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THE REACTIONS OF OXYGEN ATOMS WITH NITRATES

Final Technical Report
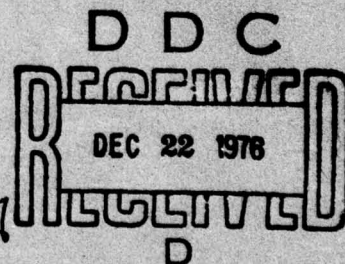
By

L.F. Salter and B.A. Thrush

8 November 1976

EUROPEAN RESEARCH OFFICE

United States Army

London, N.W.1., England.

Grant Number DAERO-75-G-020.

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20 (U) ABSTRACT

The reaction of oxygen atoms with methyl nitrate and with ethyl nitrate have been studied in a discharge-flow system at temperatures between 294 and 473 K. The initial attack involves abstraction of a hydrogen atom for which the rate expressions are shown to be 1.5×10^{10} $\exp(-22.0 \pm 1.0$ kJ mol^{-1} /RT) dm^3 mol^{-1} s^{-1} and 2.6×10^{10} $\exp(-21.6 \pm 2.6$ kJ mol^{-1}/RT) dm^3 mol^{-1} s^{-1} respectively. The activation energy for hydrogen abstraction is not reduced by the fact that the initially formed radical ruptures exothermically to yield an aldehyde plus nitrogen dioxide. The reaction mechanism and its relation to alkyl nitrate pyrolyses are discussed briefly.

THE REACTIONS OF OXYGEN ATOMS WITH NITRATES

Final Technical Report

By

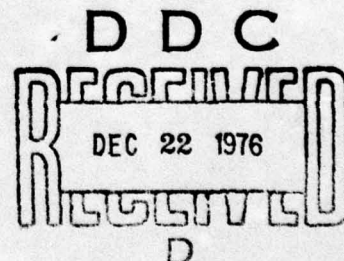**L.F. Salter   and   B.A. Thrush**

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ABSTRACT

The reaction of oxygen atoms with methyl nitrate and with ethyl nitrate have been studied in a discharge-flow system at temperatures between 294 and 473 K. The initial attack involves abstraction of a hydrogen atom for which the rate expressions are shown to be 1.5×10^{10} exp(- 22.0 ± 1.0 kJ mol^{-1}/RT) dm^3 mol^{-1} s^{-1} and 2.6×10^{10} exp(- 21.6 ± 2.6 kJ mol^{-1}/RT) dm^3 mol^{-1} s^{-1} respectively. The activation energy for hydrogen abstraction is not reduced by the fact that the initially formed radical ruptures exothermically to yield an aldehyde plus nitrogen dioxide. The reaction mechanism and its relation to alkyl nitrate pyrolyses are discussed briefly.

Contents

ILLUSTRATIONS

Introduction

Aliphatic nitrates and nitrocompounds, which are extensively used as explosives, yield a wide range of products, both under slow thermal decomposition[1-3] and under explosive conditions[4-6]. These processes clearly involve free radical reactions and, from the unstable nature of alkyl nitrates, it might be expected that chain reactions would be important. With alkyl nitrates, it is generally agreed[1,2,6] that the initial step in the pyrolysis is rupture of the $O-NO_2$ bond to yield nitrogen dioxide and a highly reactive, but thermally unstable alkoxy radical

$$CH_3ONO_2 = CH_3O + NO_2 \qquad (1)$$
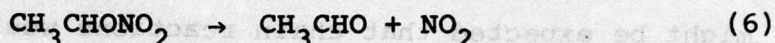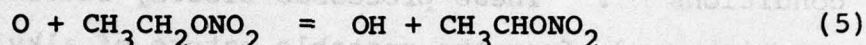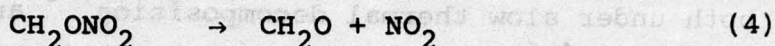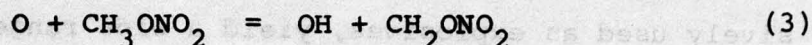
$$CH_3CH_2ONO_2 = CH_3CH_2O + NO_2 \qquad (2)$$
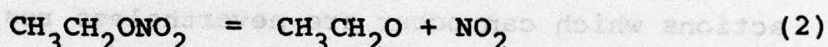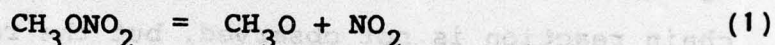
Although many of the products of the slow decomposition of alkyl nitrates would be expected to arise from the attack of alkoxy radicals on the parent molecule, Levy[2] found that ethoxy radicals generated by the pyrolysis of diethyl peroxide do not accelerate the decomposition of ethyl nitrate. This illustrates the difficulties which attend the interpretation of the nitrate pyrolyses, and no unambiguous assignment has been made of the secondary reaction steps in the pyrolysis of methyl nitrate or ethyl nitrate notwithstanding the importance of these compounds as prototype explosives.

In previous studies of the kinetics of the reaction of oxygen atoms with the related compounds methyl nitrite and ethyl nitrite, it was shown that the initial attack involved abstraction of a hydrogen atom adjacent to the nitrite group. This was followed by exoergic rupture of the molecular fragment to yield an aldehyde plus nitric oxide. By analogy, the reaction of oxygen atoms with methyl nitrate and with

ethyl nitrate would be expected to have the analogous mechanism :

$$O + CH_3ONO_2 = OH + CH_2ONO_2 \qquad (3)$$

$$CH_2ONO_2 \rightarrow CH_2O + NO_2 \qquad (4)$$

$$O + CH_3CH_2ONO_2 = OH + CH_3CHONO_2 \qquad (5)$$

$$CH_3CHONO_2 \rightarrow CH_3CHO + NO_2 \qquad (6)$$

The results presented here confirm this mechanism and thereby show that the attack of free radicals on alkyl nitrates does not lead directly to a chain reaction. This is in agreement with the kinetics of the slow pyrolysis, where a chain reaction is not observed, but the range of free radical reactions which can occur are nevertheless responsible for the complexity of the products found.

Experimental Methods

Apparatus

The reaction between oxygen atoms and methyl nitrate or ethyl nitrate was studied in a low pressure fast flow system similar to that used for the previous study[7]. This is illustrated in figure 1. The reactor consisted of a 25 mm diameter pyrex tube which passed through a copper-lined electric furnace which was 900 mm long. The furnace temperature was controlled by a Eurotherm regulator.

The reaction time could be varied by introducing the alkyl nitrate at different points along the flow tube through a grease-less movable injector system. The reagent was fed through fine Tygon tubing into a narrow-bore glass tube which terminated in a fine jet. This glass tube was slid along the flow tube by a frictional drive from a rotating shaft

which passed through a cone and socket joint.   Reaction times
of 0.02 to 1.0 s could readily be obtained with total press-
ures in the range 1 - 10 Torr.

Atomic oxygen was generated by passing ca 1% of molecular
oxygen in an argon carrier through a 200 W, 2450 MHz microwave
discharge.   Concentrations of atomic oxygen were measured
using the stoichiometric titration reaction

$$O + NO_2 = NO + O_2 \tag{7}$$

using an R.C.A. 1P28 photomultiplier cell to measure the
intensity of the air afterglow produced downstream from the
furnace exit where the flowing gases had completely cooled to
ambient temperature.   The intensity of the air afterglow is
given by

$$I = I_o [O] [NO] \tag{i}$$

When nitrogen dioxide is introduced through the mixing jet at
the furnace exit, the maximum intensity of the air afterglow
is observed when half the oxygen atoms have been converted to
nitric oxide by reaction (7).   Thus

$$I_{MAX} = I_o [O]_o^2 / 4 \tag{ii}$$

where $[O]_o$ is the initial oxygen atom concentration, providing
an absolute calibration for the photomultiplier cell based on
the titration reaction (7).   Knowing I_o, it is then possible
to measure the concentration of oxygen atoms before and after
addition of an alkyl nitrate upstream, as well as the amount
of nitric oxide formed in the decomposition of the alkyl
nitrate.   This is achieved by adding known flows of nitric
oxide at the furnace exit and using relation (i) in the form

$$I = I_o [O] ([NO]_f + [NO]_{added}) \tag{iii}$$

A plot of I against $[NO]_{added}$ is a straight line with slope $I_o[O]$, and intercept on the abscissa equal to the flow of nitric oxide emerging from the furnace $[NO]_f$.

Purification of Reagents

A commercial sample of methyl nitrate of nominal purity 99.8% was distilled at 193K, the initial and final fractions being discarded. The liquid was then subjected to several freeze-pump-thaw cycles followed by direct pumping at room temperature immediately prior to use. Ethyl nitrate was supplied by the Explosives Research and Development Establishment (Waltham Abbey) and was purified in a similar manner.

Nitrogen dioxide (Matheson) was purified by successive distillation using traps at 77K and 193K. This was continued until the solid was pure white, indicating that water and other nitrogen oxides were no longer present. It was stored in a blackened bulb.

Nitric oxide (Matheson) was purified by distillation in vacuo from 90K to 77K and from 113K to 77K through a trap containing molecular sieve and soda lime cooled to 113K.

Oxygen and argon were purified by passage through two traps at 193K and atmospheric pressure packed with glass wool followed by a similar trap at 77K and reduced pressure.

Gas flows were measured using conventional capillary flow meters: the calibration of these was based on, but did not assume, the validity of Poiseuille's Law.

Experimental Procedure

In the previous study[7] of the reactions of methyl nitrite and of ethyl nitrite with atomic oxygen, it was shown that the initial attack was the slowest step and that the

species produced reacted relatively rapidly with more atomic oxygen to yield the final products, in which the nitrogen of the initial molecule appeared solely as nitric oxide. A similar situation would be expected to obtain in the reaction of atomic oxygen with methyl nitrate or ethyl nitrate, since any nitrogen dioxide produced would rapidly be reduced to nitric oxide by the excess atomic oxygen which was invariably present

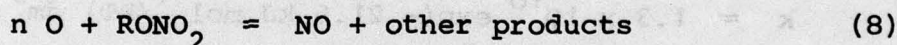$$O + NO_2 = NO + O_2 + 192 \text{ kJ mol}^{-1} \quad (7)$$
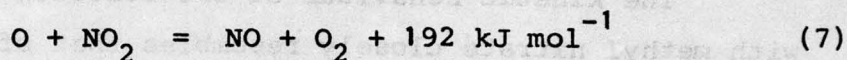
$$k_7 = 5 \times 10^9 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1} \quad (\text{ref. 8})$$

Thus measurement of the number of oxygen atoms consumed per nitric oxide molecule formed gives the stoichiometry (n) of the reaction between oxygen atoms and an alkyl nitrate. That is

$$n = ([O]_o - [O])/[NO]_f \quad (iii)$$

where the overall reaction is

$$n\, O + RONO_2 = NO + \text{other products} \quad (8)$$

Providing the subsequent reactions are rapid, the rate constant k for the initial attack of an oxygen atom on an alkyl nitrate molecule can then be derived from the integrated rate expression

$$\ln \frac{[O] [RONO_2]_o}{[O]_o ([RONO_2]_o - x)} = ([O]_o - n[RONO_2]_o)kt \quad (iv)$$

where $nx = [O]_o - [O]$.

Experimentally, it is simplest to vary the nitrate concentration for a fixed reaction time. It should be noted that any contribution by atoms or free radicals produced in the reaction

to the initial attack on the alkyl nitrate molecule will
increase the nitric oxide yield, reduce the measured stoichio-
metry n and hence increase the value of k derived from re-
lation (iv).

Results

Reaction of Oxygen Atoms with Methyl Nitrate

The kinetic behaviour of the reaction of oxygen atoms
with methyl nitrate closely resembles that of the reaction
of oxygen atoms with methyl nitrite[7].   The measured reaction
stoichiometry is close to 6 and decreases with increasing
substrate flow due to reactions between product radicals and
methyl nitrate (figure 2).

Since both the mechanisms discussed below give stoichio-
metries of n = 6, the limiting values of the rate coefficient
at low methyl nitrate concentrations were calculated for
n = 6.   These are given in Arrhenius form in figure 3, where
the best straight line corresponds to the rate expression

$$k = 1.3 \times 10^{10} \exp(- 21.6 \text{ kJ mol}^{-1}/RT) \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$$
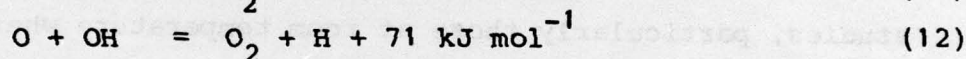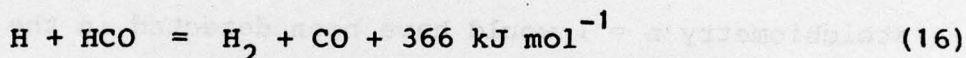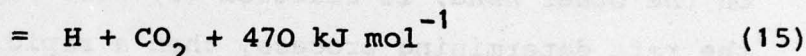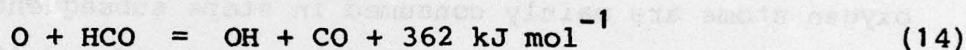
For the reaction of oxygen atoms with methyl nitrite,
a closely similar value was obtained for the corresponding
Arrhenius expression[7]

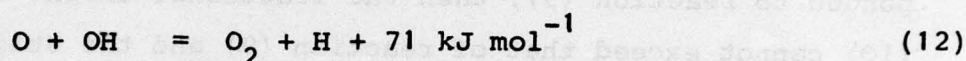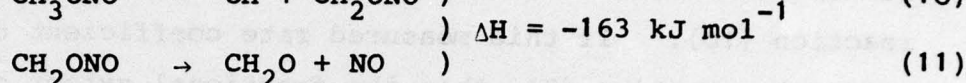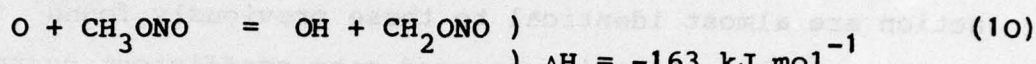$$k = 1.4 \times 10^{10} \exp(- 21.8 \pm 2.0 \text{ kJ mol}^{-1}/RT) \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$$

There are two mechanisms for the reaction between oxygen
atoms and methyl nitrate which would give the required stoichio-
metry of n = 6 and are basically consistent with the previous
results on the reaction of oxygen atoms with methyl nitrite
and other compounds[7,9,10].

If the initial step involves abstraction of an oxygen

atom from the methyl nitrate, the reaction of oxygen atoms
with methyl nitrite which has an overall stoichiometry of
n = 5 would follow :
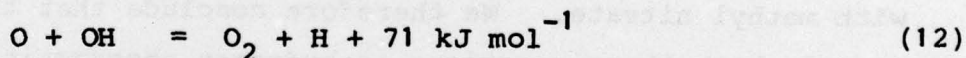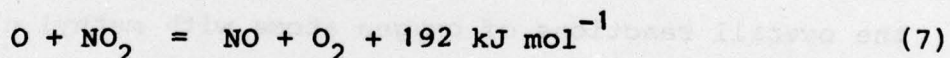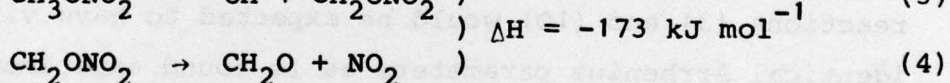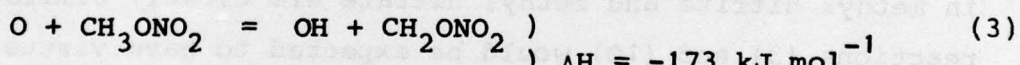
$$O + CH_3ONO_2 = CH_3ONO + O_2 + 188 \text{ kJ mol}^{-1} \tag{9}$$

$$O + CH_3ONO = OH + CH_2ONO \quad) \tag{10}$$
$$) \quad \Delta H = -163 \text{ kJ mol}^{-1}$$
$$CH_2ONO \rightarrow CH_2O + NO \quad) \tag{11}$$

$$O + OH = O_2 + H + 71 \text{ kJ mol}^{-1} \tag{12}$$

$$O + H_2CO = OH + HCO + 63 \text{ kJ mol}^{-1} \tag{13}$$

$$O + HCO = OH + CO + 362 \text{ kJ mol}^{-1} \tag{14}$$

$$= H + CO_2 + 470 \text{ kJ mol}^{-1} \tag{15}$$

$$H + HCO = H_2 + CO + 366 \text{ kJ mol}^{-1} \tag{16}$$
$$O + OH = O_2 + H + 71 \text{ kJ mol}^{-1} \tag{12}$$
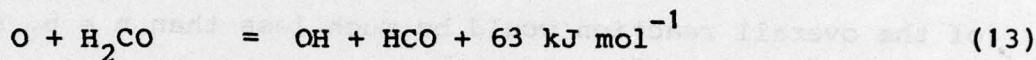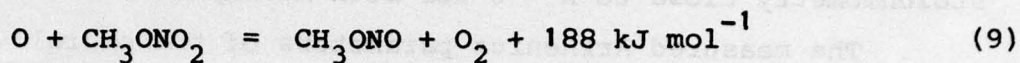
The other mechanism starts, like the methyl nitrite re-
action, with hydrogen abstraction

$$O + CH_3ONO_2 = OH + CH_2ONO_2 \quad) \tag{3}$$
$$) \quad \Delta H = -173 \text{ kJ mol}^{-1}$$
$$CH_2ONO_2 \rightarrow CH_2O + NO_2 \quad) \tag{4}$$

$$O + NO_2 = NO + O_2 + 192 \text{ kJ mol}^{-1} \tag{7}$$

$$O + OH = O_2 + H + 71 \text{ kJ mol}^{-1} \tag{12}$$

In both mechanisms, the reaction of oxygen atoms with
methyl nitrate and the subsequent steps give the stoichiometry

$$3 O + CH_3ONO_2 = CH_2O + NO + 2 O_2 + H$$
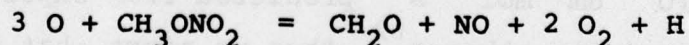
This is followed by the reaction of oxygen atoms and formalde-
hyde which goes virtually to completion since its initial
step (13) has a rate coefficient more than ten times that
found here for the reaction of oxygen atoms with methyl nitrate

$(k_{13} = 9 \times 10^7$ dm^3 mol^{-1} s^{-1} at 300K [10]). This reaction and the subsequent rapid steps (12), (14), (15) and (16) give an observed stoichiometry of n = 2.8, making the overall reaction stoichiometry close to n = 6 for both mechanisms.

The measured Arrhenius parameters of the overall reaction are almost identical to those previously found[7] for reaction (10). If this measured rate coefficient corresponded to reaction (9), then the fractional extent of reaction (10) cannot exceed that of reaction (9) and the stoichiometry of the overall reaction would be much less than n = 6, since oxygen atoms are mainly consumed in steps subsequent to (10). On the other hand, if reaction (9) were rapid and (10) were the rate determining process, then a rapid reaction with stoichiometry n = 1 would have been detected in the kinetic studies, particularly those at room temperature where reaction (10) is slow.

If, as appears highly probable, the C-H bond strengths in methyl nitrite and methyl nitrate are closely similar, then reactions (3) and (10) would be expected to have virtually identical Arrhenius parameters as is found experimentally for the overall reactions of oxygen atoms with methyl nitrite and with methyl nitrate. We therefore conclude that the initial step in both these reactions is hydrogen abstraction. For reaction (3), the A-factor found experimentally $(1.3 \times 10^{10}$ dm^3 mol^{-1} $s^{-1})$ agrees within the error limits with the value of 1.5×10^{10} dm^3 mol^{-1} s^{-1} predicted from experiments on a series of primary alkanes[12], thus we adopt that value for the A-factor giving

$$k_3 = 1.5 \times 10^{10} \exp(-22.0 \pm 1.0 \text{ kJ mol}^{-1}/RT) \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$$
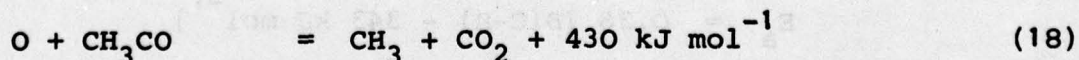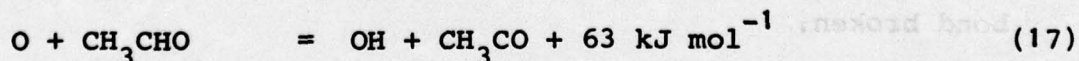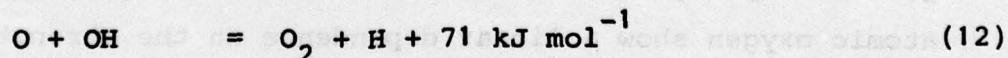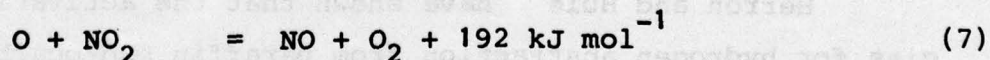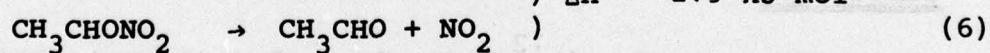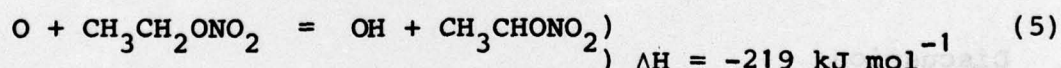
where the error limits correspond to two standard deviations of the activation energy with a predetermined A-factor.

Reaction of Oxygen Atoms with Ethyl Nitrate

As observed in the previous study of ethyl nitrite[7], the presence of an additional CH_2 group increases the number of oxygen atoms removed per initial step. Although the greater rate of the reaction of ethyl nitrate with oxygen atoms made it possible to use lower concentrations than those of methyl nitrate, the measured stoichiometries of nitric oxide production still rose quite sharply at low ethyl nitrate concentrations. These gave intercepts corresponding to n ~ 10 at zero reactant concentration as shown in figure 4. Thus the observed difference between the stoichiometries of the reactions of oxygen atoms with methyl nitrate and ethyl nitrate are the same as with the corresponding nitrites[7].

This, and the increase in rate of the initial step on passing from the methyl to the ethyl derivative, which was also observed with the nitrites[7], leads to the conclusion that the mechanism of the reaction of oxygen atoms with ethyl nitrate is strictly analogous to the reaction with ethyl nitrite, the mechanism being

$$O + CH_3CH_2ONO_2 = OH + CH_3CHONO_2 \quad) \tag{5}$$
$$CH_3CHONO_2 \rightarrow CH_3CHO + NO_2 \quad) \; \Delta H = -219 \text{ kJ mol}^{-1} \tag{6}$$
$$O + NO_2 = NO + O_2 + 192 \text{ kJ mol}^{-1} \tag{7}$$
$$O + OH = O_2 + H + 71 \text{ kJ mol}^{-1} \tag{12}$$
$$O + CH_3CHO = OH + CH_3CO + 63 \text{ kJ mol}^{-1} \tag{17}$$
$$O + CH_3CO = CH_3 + CO_2 + 430 \text{ kJ mol}^{-1} \tag{18}$$
$$O + CH_3 = H_2CO + H + 286 \text{ kJ mol}^{-1} \tag{19}$$

followed by the reaction of oxygen atoms with formaldehyde discussed above. Since $k_{17} = 3 \times 10^8 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ at 300K [11],

which is thirty times faster than the rate coefficient found here for reaction (5). The reactions of oxygen atoms with acetaldehyde and formaldehyde would go to completion on the time scale of the present experiments. The predicted overall stoichiometry for this reaction sequence is n = 10, which agrees with the measured value well within its limited accuracy.

The limiting values of the rate coefficient of the initial step at low ethyl nitrate concentrations were evaluated for n = 10. These are plotted in Arrhenius form in figure 3. As with methyl nitrate, the accuracy with which the pre-exponential factor could be determined was not high. The predicted value of 2.6×10^{10} dm^3 mol^{-1} s^{-1} for two secondary hydrogens[12] was adopted since it lay in the centre of the possible range of experimental values.

The Arrhenius expression is then

$$k_5 = 2.6 \times 10^{10} \exp(- 21.6 \pm 2.6 \text{ kJ mol}^{-1}/RT) dm^3 \text{ mol}^{-1} s^{-1}$$

Reaction (5) is more than three times faster than reaction (3), partly due to a smaller activation energy.

Discussion

Herron and Huie[12] have shown that the activation energies for hydrogen abstraction from paraffin hydrocarbons by atomic oxygen show a linear dependence on the strength of the bond broken:

$$E_a = 0.36 [D(C-H) - 343 \text{ kJ mol}^{-1}]$$

Assuming that this relation also applies to the C-H bonds in alkyl nitrates, the energies of the C-H bonds broken in the primary processes (3) and (5) must lie in the range 400 - 405 kJ mol^{-1}. As was found with methyl and ethyl nitrites, these

are normal C-H bond energies showing that the exothermic re-
organisation and fragmentation of the radical formed in (3)
and (5) occurs after hydrogen abstraction and that the poss-
ibility of such a rearrangement does not alter the Arrhenius
parameters of the process forming this radical.   It is most
unlikely that this intermediate radical could be stabilised
in the gas phase, although it could perhaps be isolated in a
matrix at low temperatures.

The conclusion reached here, that oxygen atoms attack
alkyl nitrates by hydrogen abstraction followed by decompo-
sition of the primary radical to yield nitrogen dioxide and
an aldehyde, would be expected to apply also to attack by
hydrogen atoms, hydroxyl radicals and alkoxy radicals, where
the corresponding abstraction reaction is somewhat more exo-
thermic.   With these latter species, the abstraction reaction
and rearrangement of the products yields only stable molecules.
Thus the stability of alkyl nitrates at and somewhat above
ambient temperatures is determined by a balance between the
easy fission of the RO-NO$_2$ to yield a highly reactive free
radical, and the efficient removal of such radicals when they
abstract hydrogen from the parent molecule.

On such a simplistic mechanism, the slow pyrolysis of
alkyl nitrates would be expected to the corresponding aldehyde
and alcohol plus nitrogen dioxide.   The much greater complex-
ity of the observed products arises partly from the thermal
instability, particularly of the larger alkoxyl radicals which
decompose to give smaller radicals.   Many of the observed
products undoubtedly arise from the reaction of nitrogen
dioxide with the aldehydes and alcohols produced in the de-
composition of the nitrate[1,6,13,14].   Thus the thermal de-
composition of alkyl nitrates can yield a wide range of pro-
ducts without being itself a chain process with a significant
chain length.

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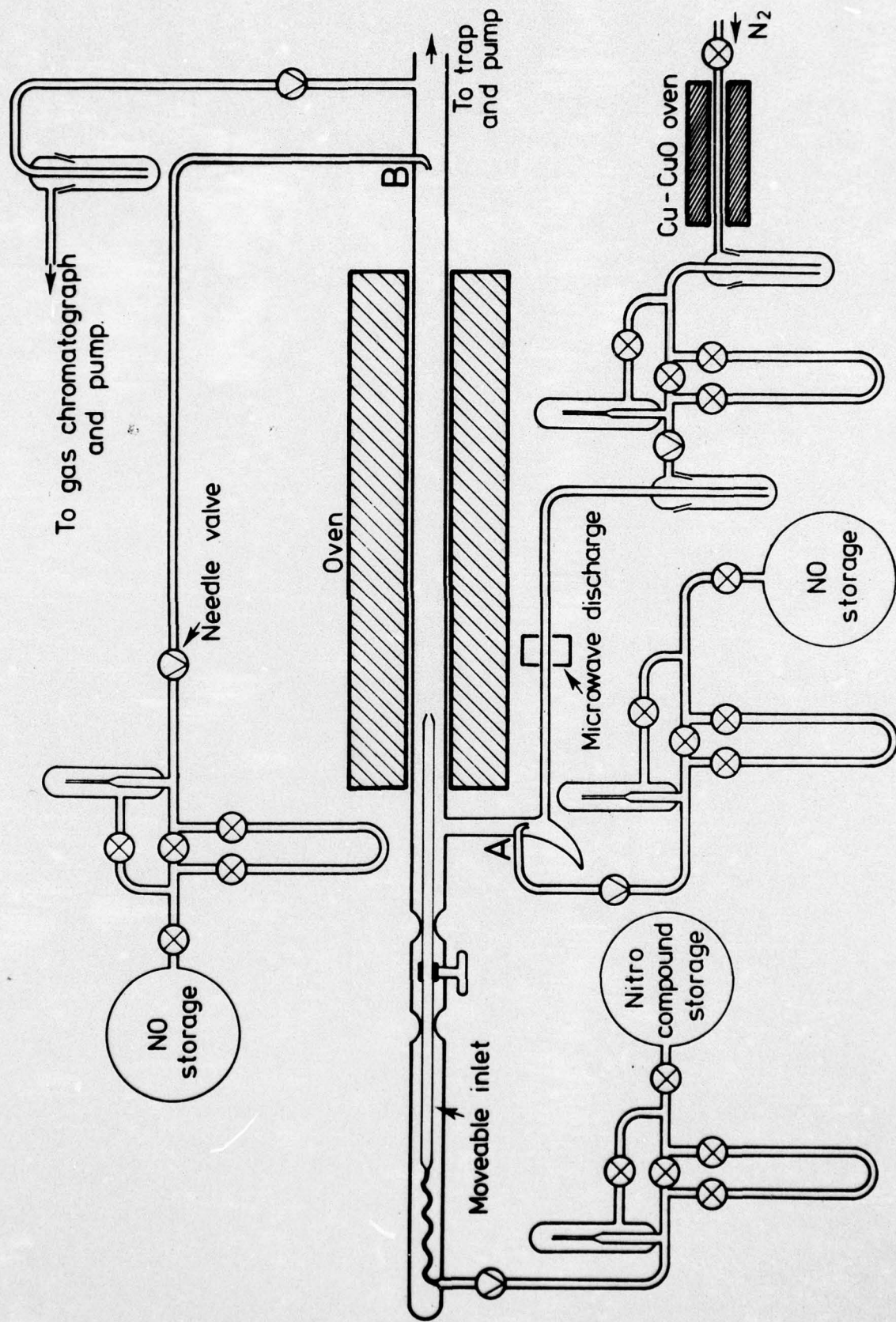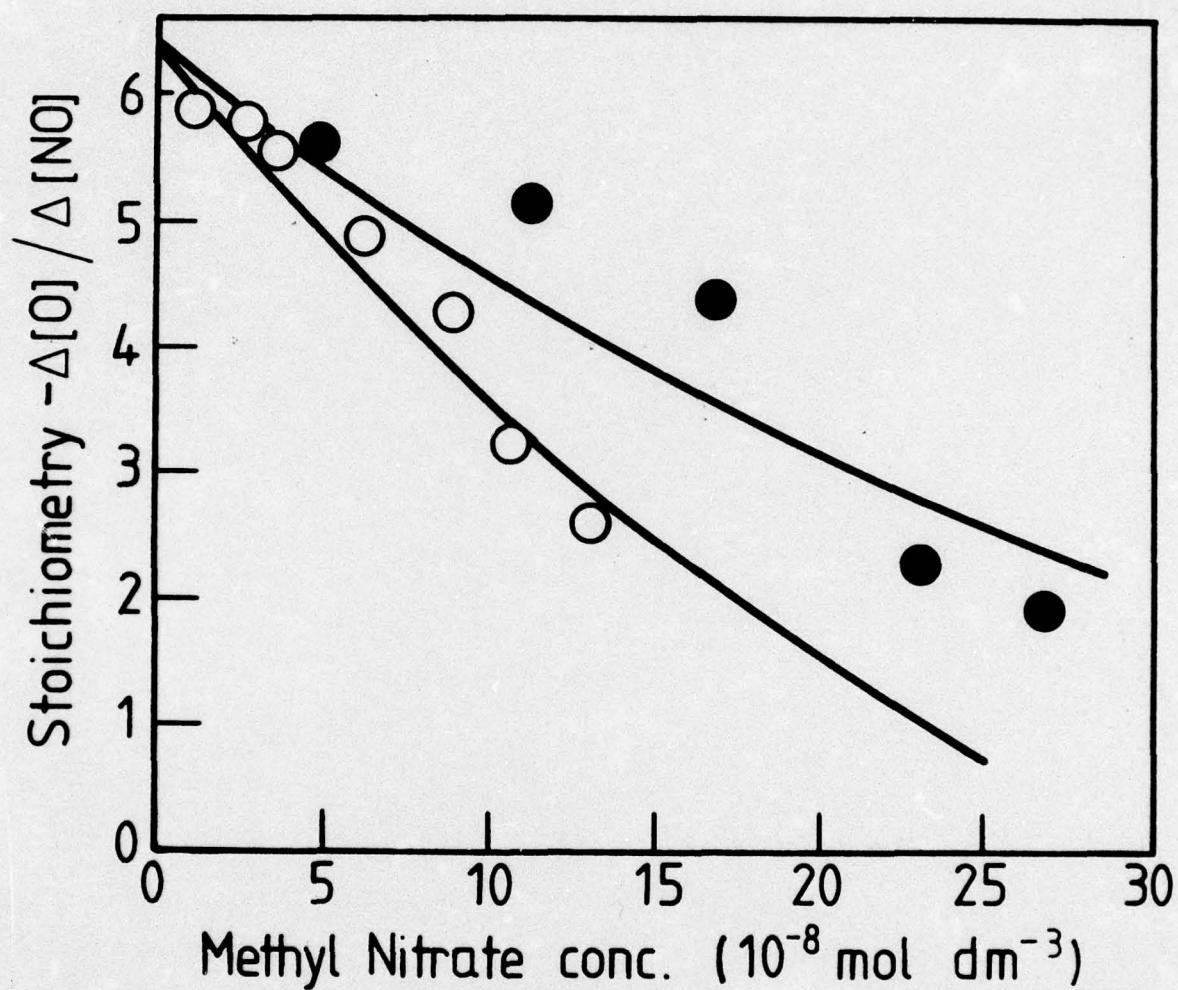
FIGURE 1 DIAGRAM OF FLOW APPARATUS.

FIGURE 2

FULL CIRCLES: 0.40s REACTION TIME AT 294.4K;
$[0]_0 = 9.5 \times 10^{-8}$ MOL DM^{-3}

OPEN CIRCLES: 0.24s REACTION TIME AT 383.2K;
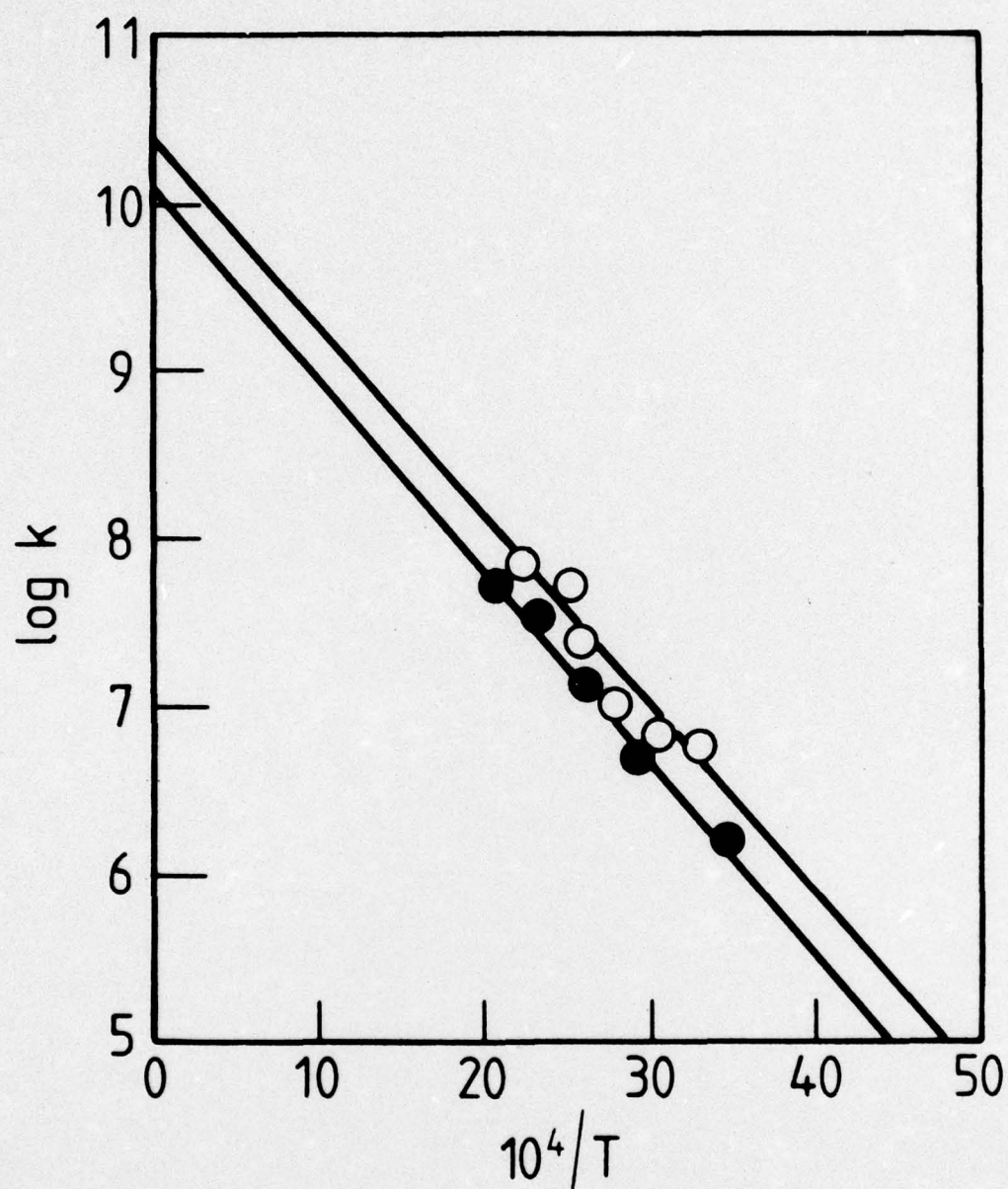$[0]_0 = 4.5 \times 10^{-8}$ MOL DM^{-3}

FIGURE 3

ARRHENIUS PLOTS FOR OXYGEN ATOM ATTACK

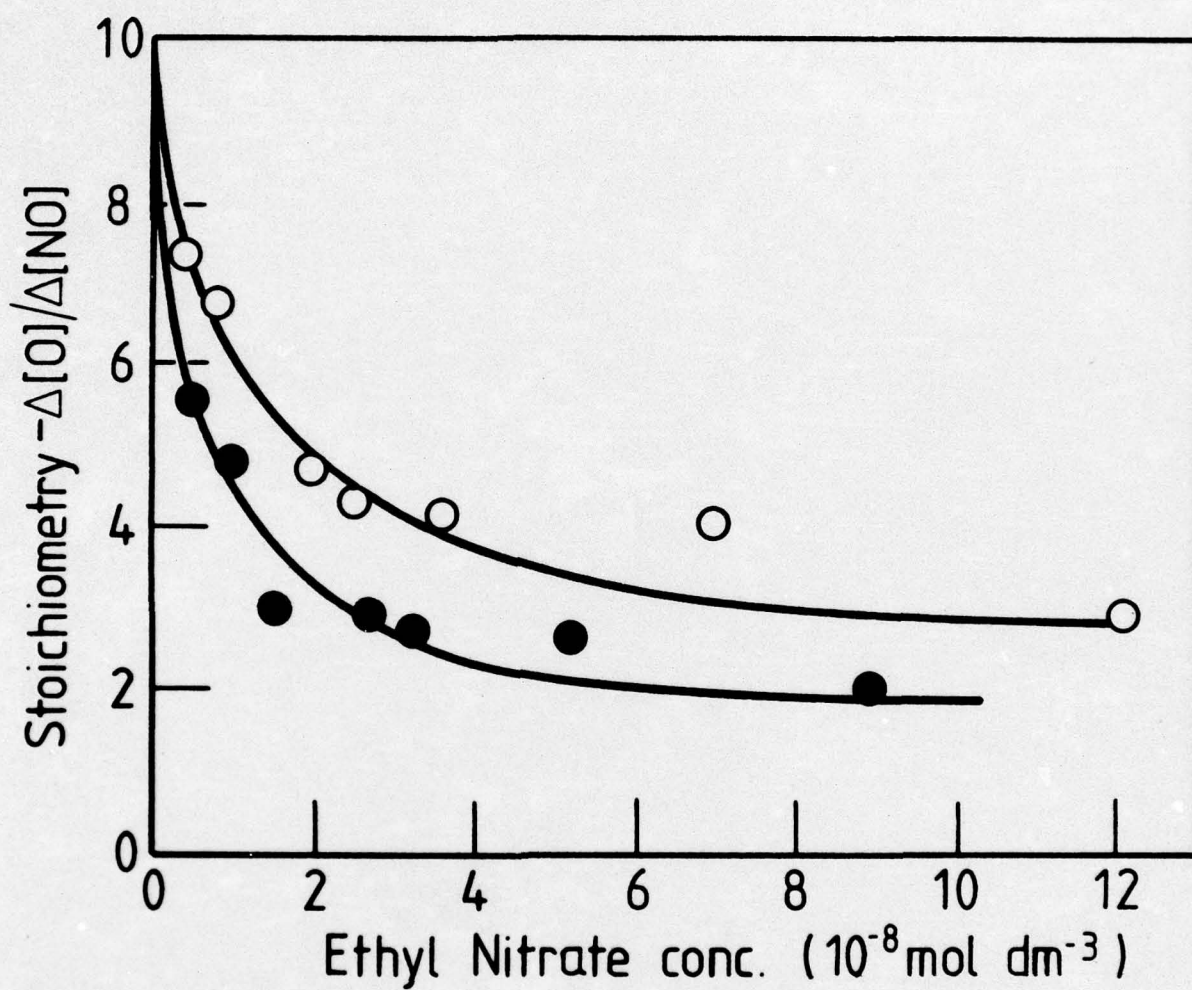FULL CIRCLES: METHYL NITRATE

OPEN CIRCLES: ETHYL NITRATE

FIGURE 4

FULL CIRCLES: 0.30s REACTION TIME AT 300.2K;
$[O]_0 = 2.7 \times 10^{-7}$ MOL DM^{-3}

OPEN CIRCLES: 0.25s REACTION TIME AT 333.2K;
$[O]_0 = 2.5 \times 10^{-7}$ MOL DM^{-3}